Abstract

MEASURING THE PERFORMANCE OF RECENT GENERALIZED GRADIENT APPROXIMATIONS TO DENSITY FUNCTIONAL THEORY IN MOLECULES AND SOLIDS.

Density functional theory is a successful theory used in physics, chemistry and nanoscience to describe the ground state properties of solids and molecules. It calculates ground state energies and related properties by using the density of the valence electrons as a fundamental variable. In a system of interacting electrons, the electrons will correlate due to the Pauli exclusion principle, as well as their coulomb repulsion. This interaction energy is known as the exchange-correlation energy and is approximated in density functional theory because it is the only unknown in the energy as a functional of density. The simplest model to approximate this exchange-correlation energy is the local density approximation, which only relies on the local density of the valence electrons at every point. Generalized gradient approximations are approximations which build upon the local density approximation by also using the gradient of the local density. Recently, many new versions of the generalized gradient approximation have been developed to attempt to obtain better energetic and structural properties either at the same time, or at the expense of the other. In this study, we examine the performance of these models by calculating the atomization energy of the AE6 test set. The cohesive energy, lattice constant and bulk modulus of a four solid test set was also calculated. These calculations were done using ABINIT, a density functional theory code that uses a pseudopotential model with plane waves to examine molecules and solids. One of the more recently developed generalized gradient approximation models, the SOGGA, is tested to compare with the standard models. The accuracy of using a pseudopotential model is also tested. It was found that by using a generalized gradient approximation that was better for energy calculations, the structural property calculations would not be as accurate. The SOGGA is a functional that approximates structural properties of solids accurately but does not calculate energies as well. It was also found that using a pseudopotential model resulted in a 1% difference from the all electron calculations.